

# Combinatorial Optimization of Transparent Conducting Oxides (TCOs) for PV

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# COMBINATORIAL OPTIMIZATION OF TRANSPARENT CONDUCTING OXIDES (TCOS) FOR PV

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## ABSTRACT

Transparent conducting oxides (TCOs) can serve a variety of important functions in thin film photovoltaics such as transparent electrical contacts, antireflection coatings and chemical barriers. Two areas of particular interest are TCOs that can be deposited at low temperatures and TCOs with high carrier mobilities. We have employed combinatorial high-throughput approaches to investigate both these areas. Conductivities of  $\sigma = 2500 \Omega^{-1}\text{-cm}^{-1}$  have been obtained for In-Zn-O (IZO) films deposited at 100 °C and  $\sigma > 5000 \Omega^{-1}\text{-cm}^{-1}$  for In-Ti-O (ITiO) and In-Mo-O (IMO) films deposited at 550 °C. The highest mobility obtained was 83  $\text{cm}^2/\text{V}\cdot\text{sec}$  for ITiO deposited at 550 °C.

## INTRODUCTION

Transparent conducting oxides (TCOs) can serve a variety of important functions in thin film photovoltaics such as transparent electrical contacts, antireflection coatings and chemical barriers [1]. Two areas of particular interest are TCOs that can be deposited at low temperatures and TCOs with high carrier mobilities. In this study, we report on new high performance  $\text{In}_2\text{O}_3$ -based materials substituted separately with Zn, Mo, and Ti [2-6]. We have employed combinatorial high-throughput approaches to investigate these materials [2,3,7].

## EXPERIMENTAL APPROACH

Compositionally graded samples ("libraries") are deposited by co-sputtering onto 2"x2" glass substrates [8]. Three to five libraries are generally required to cover the full composition range for a binary tie-line, such as from  $\text{In}_2\text{O}_3$  to ZnO. After deposition and, in some cases, additional controlled atmosphere annealing, the libraries are characterized by a variety of automated combinatorial mapping tools. At present, these include EPMA for metals stoichiometry, linear 4-point probe for sheet resistance [2], UV/VIS/NIR (200 - 2000 nm) reflection and transmission, FTIR optical reflection and transmission (1.8 – 25  $\mu\text{m}$ ) [9] and x-ray diffraction (XRD) using a large-area 2D detector [3]. For selected libraries, smaller samples are cut out for Hall effect measurements to determine the carrier concentration and mobility.

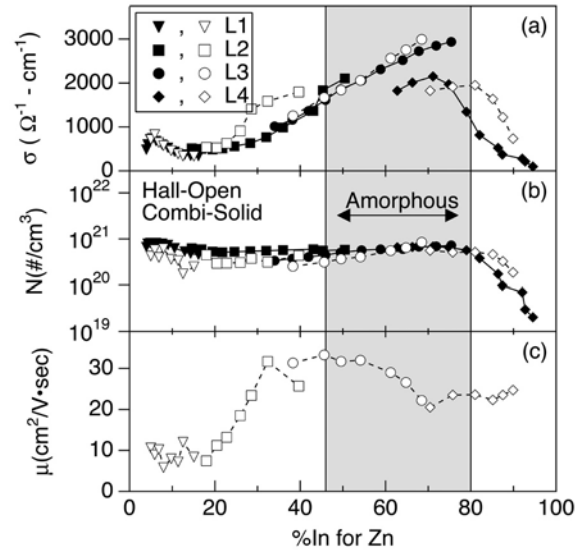


Fig. 1. Electrical conductivity (a), carrier concentration (b) and mobility (c) for In-Zn-O (IZO) deposited at 100 °C. Solid symbols are for data taken using automated combinatorial tools and open symbols are for data taken using a conventional Hall effect probe on individual cut out pieces.

## RESULTS AND DISCUSSION

### In-Zn-O (IZO)

For In-Zn-O (IZO) libraries deposited from ceramic oxide targets at 100 °C in Ar with no post-deposition annealing, a broad maximum in the conductivity with  $\sigma \approx 2500 \Omega^{-1}\text{-cm}^{-1}$  is found for  $x \sim 0.55$  to  $0.75$  in  $\text{Zn}_{1-x}\text{In}_x\text{O}_y$  (Fig. 1a). This roughly correlates with the composition range found to be amorphous by the XRD mapping. For higher In content, the carrier concentration decreases (Fig 1b) and for lower In content, the mobility decreases (Fig 1c). In Fig 1b, the combinatorially measured carrier concentration (solid symbols) is determined from the measured optical reflection and transmission spectra as described below. For samples with a composition in the amorphous region, the conductivity is unchanged by annealing for one

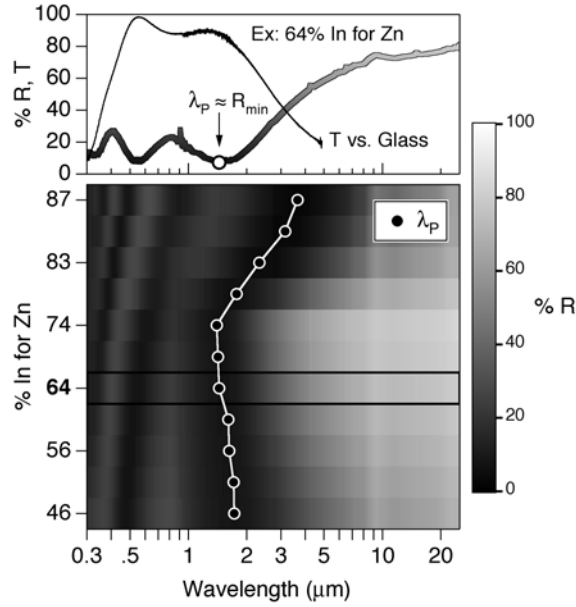


Fig. 2. Optical reflectance spectra for In-Zn-O (IZO) deposited at 100 °C. Top panel: Example spectra for one spot. Bottom panel: Reflectivity spectra for 11 compositions displayed using gray scale. The overlaid open white circles show the wavelength for  $R_{\min}$  which approximately corresponds to  $\lambda_p$ .

hour in air at 200 °C. Figure 2 shows the optical reflectivity from 0.3 to 25  $\mu\text{m}$  for an IZO library compositionally centered on the conductivity maximum. These samples are transparent in the visible region as evident from the spectra shown in the top panel and, in both panels, the overlaid open circles show the approximate plasma wave-

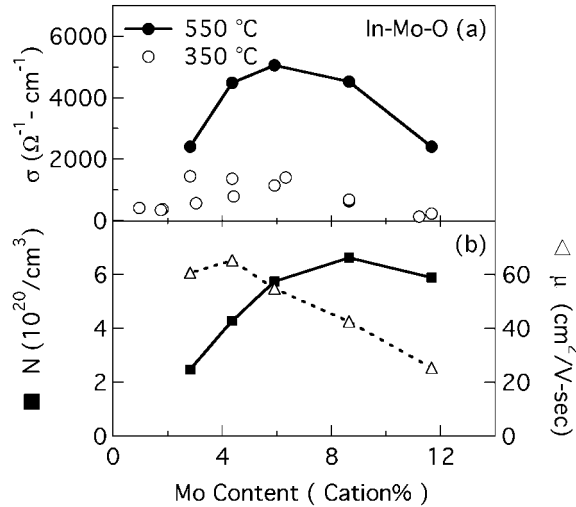


Fig. 3. Electrical conductivity (a), carrier concentration (b, left) and mobility (b, right) for In-Mo-O (IMO) for samples deposited at 350 °C and 550 °C.

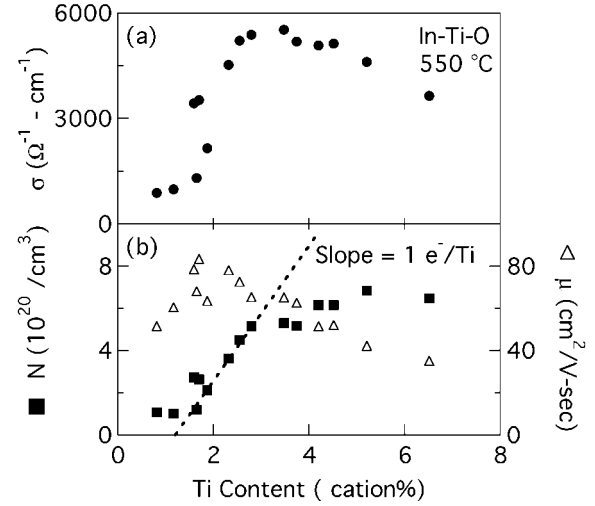


Fig. 4. Electrical conductivity (a), carrier concentration (b, left) and mobility (b, right) for In-Ti-O (ITiO) samples deposited at 550 °C.

length ( $\lambda_p$ ). For most TCOs, the infrared optical properties are well described by a simple free-carrier (Drude) model [9] in which

$$\lambda_p \propto \sqrt{\frac{m^*}{N}} \quad (1)$$

where  $m^*$  is the electron effective mass and  $N$  is the electron carrier concentration. Hence, from the composition dependence of  $\lambda_p$  (Fig. 2, bottom panel) one can determine the composition dependence of the carrier concentration across an entire library without having to cut the library into pieces for individual Hall measurements (Fig 1b.).

#### In-Mo-O (IMO)

For In-Mo-O (IMO) libraries deposited at 350 °C, a maximum in the conductivity with  $\sigma \approx 1000 \Omega^{-1}\text{-cm}^{-1}$  is found for ~ 6% Mo in place of In (Fig. 3a). Increasing the deposition temperature to 550 °C results in a five fold increase in the maximum conductivity to  $\sigma \approx 5000 \Omega^{-1}\text{-cm}^{-1}$ . This is due to increases in both the carrier concentration and the mobility (Fig. 3b). In particular, for IMO samples grown at 550 °C, the maximum mobility obtained is 65  $\text{cm}^2/\text{V-sec}$  at ~ 4% Mo and the maximum carrier concentration is  $6.6 \times 10^{20}/\text{cm}^3$  at ~ 8.5% Mo.

#### In-Ti-O (ITiO)

In addition, In-Ti-O (ITiO) has been investigated for use as a high mobility TCO (Fig. 4). For ITiO libraries deposited at  $T_s = 550 \text{ }^\circ\text{C}$ ,  $\sigma \approx 5000 \Omega^{-1}\text{-cm}^{-1}$  for ~ 3 to 4 % Ti in place of In with a maximum mobility of 83  $\text{cm}^2/\text{V-sec}$  at ~ 2 % Ti. For the sputtered ITiO samples, there is a

linear increase in the carrier concentration of  $3.4 \times 10^{20}/\text{cm}^3$  per %Ti from  $\sim 1.5$  to 3 % Ti. This corresponds to 1.06 electrons / Ti indicating that for these growth conditions, Ti is a very effective dopant for  $\text{In}_2\text{O}_3$  contributing the expected 1 electron per dopant atom for Ti doping of  $\text{In}_2\text{O}_3$ . For comparison, in IMO films grown by pulsed laser deposition (PLD), Mo-doping yields  $\sim 0.2 - 0.3$  electrons / Mo [5].

### SUMMARY

We have employed combinatorial high-throughput approaches to investigate both these areas. Conductivities of  $\sigma = 2500 \Omega^{-1}\text{-cm}^{-1}$  have been obtained for In-Zn-O (IZO) films deposited at  $100^\circ\text{C}$  and  $\sigma > 5000 \Omega^{-1}\text{-cm}^{-1}$  for In-Ti-O (ITiO) and In-Mo-O (IMO) films deposited at  $550^\circ\text{C}$ . The highest mobility obtained was  $83 \text{ cm}^2/\text{V-sec}$  for ITiO deposited at  $550^\circ\text{C}$ . Hence, IZO films should work well for applications requiring low-temperature deposition and processing such as TCO coatings onto flexible polymer substrates. Whereas, either IMO or ITiO films should work well for applications requiring a high carrier mobility such as devices requiring optical transparency in the infrared.

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